Ternary System Nicotine-Water-Kerosene

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A three-phase system was noted in previous work on the distribution of nicotine between water and kerosene. This study was undertaken to determine whether a highly concentrated nicotine phase could be obtained by proper balance of solvent volumes and temperature within the range normally used for recovery of nicotine.

The behavior of the ternary system at various temperatures is described. Phase diagrams of the system at 64°, 67°, and 70° C. are given. A partial space model plotted from the data shows the conditions under which three phases exist.

A highly concentrated nicotine phase can be produced. The ratio of solvents and temperature required to produce such a phase is out of the range normally used for recovery of nicotine.

DURING studies at this laboratory on distribution of nicotine between water and kerosene (*1*), occasionally a three-phase system was observed. This system was studied more closely in the hope that it might afford a means of obtaining a nicotine-rich phase from dilute aqueous nicotine solutions which would be useful in a process for recovery of nicotine. Time was not available for collection of data on the complete system, but it was decided that the data on hand should be reported for reference purposes.

PROCEDURE

A 52-ml. glass-jacketed buret was connected to a constant temperature bath. The buret was fitted with a thermometer and water was pumped through the jacket by means of a small centrifugal pump. Fifteen milliliters of an aqueous nicotine solution were placed in the buret and 15 ml. of kerosene were added. The kerosene was Deobase—a commercial, specially purified, and deodorized grade. The nicotine was purified by vacuum distillation. The buret was stoppered and rocked at a constant temperature for 15 minutes to establish equilibrium. It was then set in an upright position to allow separation of the layers. Two or three phases formed and the volumes of the phases were recorded.

A new temperature was selected and the buret was again set in motion. Observations were made on the phases existing at this temperature. The process was repeated until the system passed from two-phase to three-phase and back to two-phase again. The transition temperatures were recorded.

At certain temperatures the three phases were separated by drawing them off through a stopcock on the buret and their compositions were determined. Nicotine was determined by the silicotungstic acid procedure, water by the Karl Fischer method, and kerosene by difference. Nicotine was found to exhibit no interference to the determination of water by the Karl Fischer reagent.
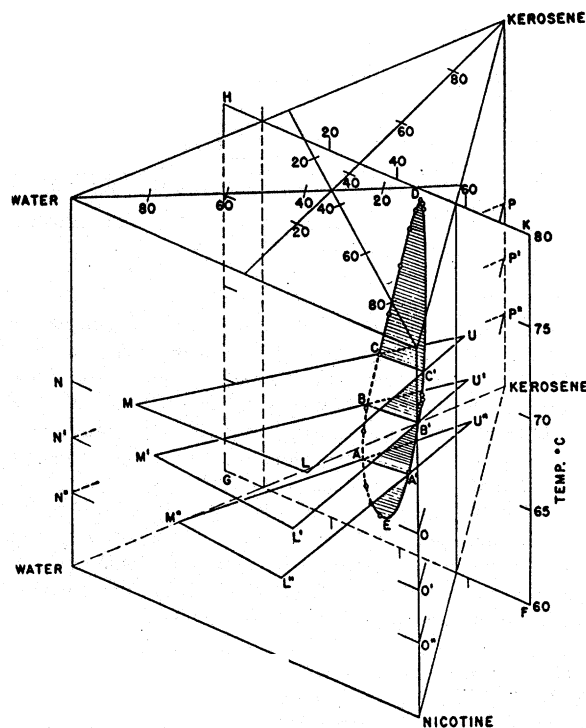

Figure 1. Partial Space Model Diagram of the Three-Component System: Nicotine-Water-Kerosene

DISCUSSION

Figure 1 is a partial space model diagram of the three-component system—nicotine-water-kerosene. The apexes represent

TABLE I. COMPOSITION AND VOLUME OF PHASES

Original Composition of System		Composition of Phases at Equilibrium			Observed Volumes of Phases at Equilibrium[a]		
	Wt. %[b]	Upper, wt. %	Middle, wt. %	Lower, wt. %	Upper, ml.	Middle, ml.	Lower, ml.
		At 70° C.					
V. Nicotine	37.64	38.66	16.24	62.68			
Water	18.53	0.75	83.01	33.74	23.7	4.7	2.5
Kerosene	43.82	60.59	0.75	3.58			
		At 67° C.					
W. Nicotine	33.70						
Water	22.47				22.45	6.35	1.9
Kerosene	43.82						
X. Nicotine	37.64	35.66	19.35	59.76			
Water	18.53	0.63	75.43	38.89	22.5	4.0	4.3
Kerosene	43.82	63.71	5.22	1.35			
Y. Nicotine	41.57						
Water	14.60				22.6	1.9	6.3
Kerosene	43.82						
		At 64° C.					
Z. Nicotine	37.64	32.74	24.55	53.73			
Water	18.53	0.48	70.11	45.63	21.5	2.4	6.7
Kerosene	43.82	66.78	5.34	0.64			

[a] Volume at room temperature was 30 ml. Apparent increase in total volume was due to expansion at higher temperatures.
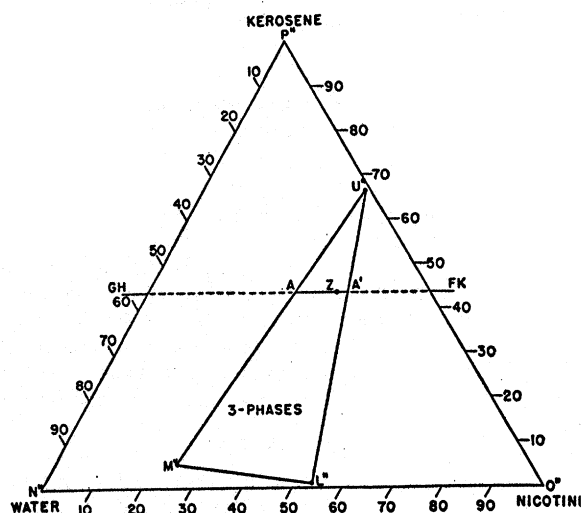[b] Wt. % of sum of all three components.
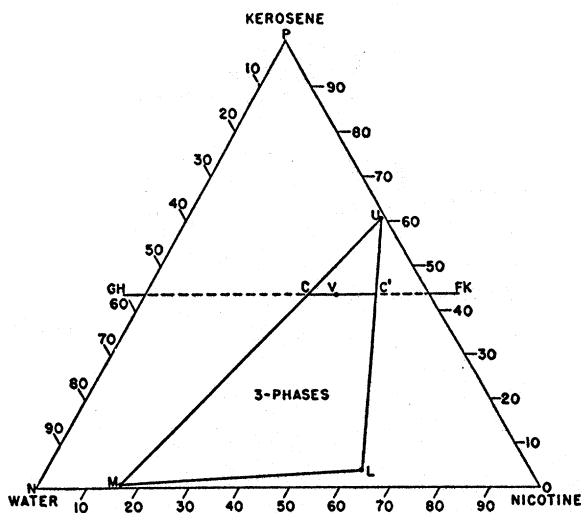
Figure 2. Phase Diagram of Three-Component System at 70° C.
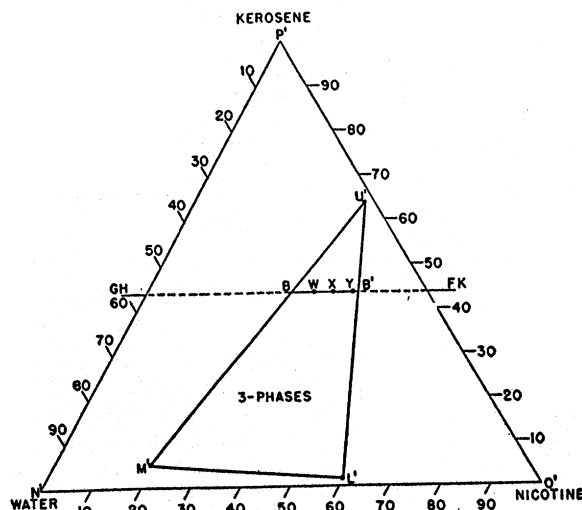
Figure 3. Phase Diagram of Three-Component System at 67° C.

Figure 4. Phase Diagram of Three-Component System at 64° C.

100% of any one component. Plane *FGHK* cuts vertically through the triangular prism at 43.82% kerosene. Temperature is represented on the vertical axis and the percentage of nicotine on the horizontal axis. Planes *NPO*, *N'P'O'*, and *N"P"O"* are normal to plane *FGHK* at 70°, 67°, and 64° C., and lines *CC'*, *BB'*, *AA'* are at the intersections of these planes, respectively. The points *M*, *U*, and *L* lie on plane *NPO*; *M'*, *U'*, and *L'* are on plane *N'P'O'*; and *M"*, *U"*, and *L"* are on plane *N"P"O"*. The enclosed curve *ABCDC'B'A'E* on the 43.82% kerosene plane, *FGHK*, represents a vertical cross section of a solid figure, a portion of which is represented by *MULM"U"L"*, and its periphery represents the transition points from two to three phases in this plane.

Three phases exist in equilibrium within the solid figure *MULM"U"L"*. The composition of an upper phase at any particular temperature is represented by a point on the line *UU"* at that temperature. Similarly, the compositions of a middle phase and a lower phase are represented by a point on the lines *MM"* and *LL"*, respectively. Only one or two phases can exist outside the solid figure partially shown here.

Table I gives the original composition of the over-all system, the composition of each phase, and the observed volume of each phase. These weight per cent compositions are plotted on the three plane figures *NPO*, *N'P'O'*, and *N"P"O"*. For simplicity and accuracy these planes are shown separately in Figures 2, 3, and 4, respectively.

Figure 2 is a phase diagram at 70° C. A system of the composition represented by point *V* was heated to this temperature, whereupon it separated into three phases. Analyses of the three phases were made for each component as shown in Table I. The composition of the upper phase is represented by point *U*, the middle phase by point *M*, and the lower phase by point *L*. Similarly, systems of compositions *W*, *X*, and *Y* in Figure 3 gave phases of compositions *U'*, *M'*, and *L'* at 67° C., and the composition *Z* in Figure 4 gave phases of compositions *U"*, *M"*, and *L"*. At 64° C. the three compositions represented by *S*, *X*, and *Y* in Figure 3 and shown in Table I were chosen to illustrate the changes in volume of the phases with composition at 67° C.

Between temperatures of 64° and 70° C., the upper phase consists of a 32 to 39% nicotine solution in kerosene with very little water. The middle phase consists mainly of a 16 to 25% nicotine solution in water with a small amount of kerosene. The lower phase consists of a 34 to 45% solution of water in nicotine with very little kerosene.

The bulk of the nicotine available in the ternary system is found in the upper or kerosene-rich phase. The amount of nico-

tine in this phase is not as great as the amount of nicotine found in the phase containing the bulk of the nicotine in the two-phase water-nicotine system (*2*). Only a trace of water is present in the kerosene-rich phase of the ternary system. In cases where water is undesirable, the ternary system offers an advantage over the two-phase water-nicotine system where water is present in both phases in appreciable amounts.

Any system of a composition represented by the three-phase

TABLE II. OBSERVED TRANSITION TEMPERATURES FROM TWO TO THREE PHASES

Nicotine in System[a], %	Transition Temps., ° C.	
46.70	75.5	75.5
46.08	79.0	68.6
45.80	79.3	68.9
45.52	79.5	68.4
44.96	79.4	68.1
43.84	78.9	66.0
42.15	77.6	64.4
39.34	75.3	62.5
37.43	73.4	61.6
36.53	72.5	61.3
33.72	70.0	61.2
30.91	67.4	61.7
29.79	66.8	62.5
28.66	65.5	65.5

[a] Kerosene held constant at 43.82%.

triangles of Figures 2, 3, and 4 will separate into three phases of compositions represented by the apexes of these triangles.

According to Gibb's phase rule, $F = C - P + 2$, there can be 4 degrees of freedom for any single phase and as temperature and pressure are fixed, the concentration of two of the three components in the phase adequately describes the system. Within the solid figure in Figure 1 where three phases exist there can be 2 degreees of freedom, and as pressure is fixed temperature adequately describes the system.

Table II shows the observed transition temperatures between two and three phases. These were used to plot the closed curve $ABCDC'B'A'E'$ shown in the space model.

LITERATURE CITED

(1) Claffey, J. B., Badgett, C. O., Skalamera, J. J., and Phillips, G. W. M., IND. ENG. CHEM., 42, 166–71 (1950).
(2) Hudson, C. S., Z. physik. Chem., 47, 113 (1903).